Application of Environmental Fate Modeling to
HERTG HPV Group 1 - Alkyl Sulfides Category

This document provides a short evaluation of the EQC computer model, which was used to assess the fate and distribution, and hence environmental concentrations, of selected members of the HERTG Group 1, alkyl sulfides.

The US EPA has agreed that computer modeling techniques are an appropriate approach to estimating chemical partitioning and distribution in the environment. Specifically, fugacity based, multimedia fate modeling can be applied to compare the relative distribution of chemicals between environmental compartments (i.e., air, soil, water, suspended sediment, sediment, biota). A widely used model for this approach is the EQC model (1). EPA cites the use of this model for this purpose in its document titled *Determining the Adequacy of Existing Data,* prepared for the HPVC program.

There are three "levels" of the EQC model. In its document, EPA states that it accepts Level I fugacity modeling to estimate transport/distribution values. In the same document EPA states that Level III model data are considered "more realistic and useful for estimating a chemical's fate in the environment on a regional basis". However, the selection and application of any one of the three models should not be done without considering their appropriateness for use with chemical(s) of interest. This includes a basic understanding of selected physical/chemical properties of the chemicals to be modeled, as well as the model.

The EQC Level I model utilizes input of the basic chemical properties of molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. The EQC Level II model also calculates the rates of transport (advection) and degradation within the environmental compartments. Application of the level II model requires data on the rates of biodegradation, hydrolysis, photolysis, and oxidation. EQC Levels I and II were used for this evaluation. EQC Level III evaluates the effects of discharge rates to air, water, and soil and intermedia transport rates. EQC Level III was not conducted for the present evaluation since the physical properties of the chemicals will not result in emissions or transport to air or water.

Since many of the basic physical properties and degradation rates of this class of chemicals are likely to be unavailable, another model was needed to estimate physical/chemical properties from structure. The model used for this purpose was EPIWIN, version 3.02 (2), which is also used by the EPA and was developed jointly with Syracuse Research Corporation. EPIWIN includes algorithms for estimation of all properties and rates needed for the application of EQC.

Five basic chemical structures were utilized for this evaluation and these are shown in Figure 1 (JRC document). Not all possible structures were modeled since this is a scoping evaluation, but for a number of chemicals, the high and low ends of molecular weight range were evaluated in the models, as was the difference in results between mono- and di-sulfide links. In all, the

basic physical properties of over a dozen structures were estimated using EPIWIN and 9 of these are shown in Table 1. The program worked with the particular sulfur compounds and molecular weight ranges tested and produced estimates for each structure. Inspection of the results in Table 1 indicates that all of these compounds have very low water solubility and low volatility. They also have very high log K_{ow} values. This is not unexpected, however, it should be cautioned that, at least for the high molecular weight compounds, these properties are likely to be outside the range of the training and validation data sets for which the model was developed. As a result, values like a log K_{ow} of 20 are likely to be indicative, rather than quantitatively accurate. However, the results appear to be directionally correct; that is to say, it is expected that these compounds will be virtually in-soluble and non volatile, and strongly bound to organic carbon. The EPIWIN model also has a cut-off limit for the bioconcentration (BCF) of high molecular weight chemicals. Not shown in Table 1, but used in producing the EQC model, are rate estimates for photochemically catalyzed air oxidation and for aquatic biodegradation. Due to strong binding to soil, soil biodegradation rates were assumed to be negligible. In addition, the model predicts negligible hydrolysis for these chemicals.

Results of EQC Level I modeling are shown in Table 2. All of the structures evaluated have essentially the same environmental distribution: 100% goes to soil and sediment (the relative percentages merely reflect the relative available volumes of these compartments). Only the 2-propanol derivative (CAS# 67124-09-8) shows any significant water solubility, resulting in an aqueous distribution of 0.4%. That chemical and the sulfurized 1-decene compound (CAS# 72162-15-3) were low enough in molecular weight to have any associated volatility, resulting in 0.2% partitioning to air. These results are not unexpected. Based on physicochemical properties, it is expected these chemicals will partition strongly to soil and sediment. Table 3 shows results of EQC Level II modeling. The linear molecules (CAS#s 72162-15-3 and 67762-55-4) had considerable predicted biodegradability. All of the chemicals were predicted to air oxidize rather quickly (half-lives of a few hours), however, for the higher molecular weight species this fate was limited due to low volatility. So, in general terms, the major (and only) effective removal mechanism for these chemicals is air oxidation. For the high molecular weight chemicals, e.g. MW ~ 400 and higher, this mechanism is slow and consequently the chemical is advected out of the region before more than a few percent are degraded.

In conclusion, it is evident that EQC modeling may be conducted on this class of additives. Additionally, the EPIWIN model may be used to estimate the physical properties and degradation rates of these chemicals which are needed for input into the EQC model. Results of fugacity modeling show that molecules that comprise the alkyl sulfides are expected to partition almost exclusively to soil and sediment. They also would not be expected to migrate appreciably as indicated by high log K_{oc} values. Although the results of this modeling are consistent with the expected behavior of these chemicals, the exact values of the physical properties are somewhat suspect when applied to the very high molecular weight members of this group.

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HERTG HPV Group 1 - Alkyl Sulfides Category

References

1. Mackay, D., A. Di Guardo, S. Paterson, and C. Cowan. 1996. Evaluating the Environmental fate of a Variety of Types of Chemicals using the EQC Model. Environ. Toxicol. Chem. 15:1627-1637.

2. EPIWIN. 1999. Estimation Program Interface for Windows, version 3.02. Syracuse Research Corporation, Syracuse, NY, USA.

Application of Environmental Fate Modeling to
HERTG HPV Group 1 - Alkyl Sulfides Category

Table 1: Physical Properties of Representative Structures of Alkyl Sulfides as Modeled by EPIWIN

CAS #	N	Molecular Weight	Log K_{ow}	Water Solubility (mg/L)	Vapor Pressure (Pa)	Log K_{oc}	Log Bio-concen-tration Factor	Melting Point (°C)	Boiling Point (°C)	Atmospheric Oxidation	
										OH^- Rate Constant (cm^3/molec-sec)	Half-life (hrs)
67124-09-8	Monomer	260.5	5.43	0.475	5.89E-03	3.00	3.48	68.15	302.85	23.32	5.51
72162-15-3	Dimer, S	314.6	9.61	6.23E-05	7.11E-03	6.04	0.5	58.01	353.69	58.85	2.18
72162-15-3	Dimer, SS	346.7	10.57	6.15E-06	5.60E-04	6.31	0.5	88.67	386.95	282.15	27.30
68511-50-2	y=3	410.8	7.99	3.94E-04	3.71E-05	6.12	3.45	147.52	409.48	35.69	3.60
68511-50-2	y=8	851.6	15.23	3.29E-18	3.63E-16	11.98	0.5	329.32	749.88	90.67	1.42
68515-88-8	y=1	402.8	10.65	2.35E-06	3.56E-04	6.49	0.5	128.08	377.79	18.94	6.78
68515-88-8	y=4	835.6	20.56	1.20E-17	4.40E-14	12.74	0.5	186.87	477.56	46.69	2.75
67762-55-4	y=2.5, x=1	497.0	16.00	1.64E-11	5.69E-08	9.50	0.5	186.92	504.54	77.22	1.66
67762-55-4	y=2.5 x=2	529.0	16.95	1.59E-10	3.90E-09	9.77	0.5	213.83	537.80	300.52	22.63

Table 2: Environmental Distribution of Representative Structures of Alkyl Sulfides as Modeled by EQC Level I

CAS#	N	Air (%)	Water (%)	Soil (%)	Sediment (%)	Suspended Sediment (%)	Biota (%)	Fugacity (µPa)
67124-09-8	Monomer	0.265	0.407	97.1	2.158	0.067	5.48E-03	0.025
72162-15-3	Dimer, S	0.196	2.70E-05	97.6	2.168	0.068	5.51E-03	0.015
72162-15-3	Dimer, SS	0.019	2.97E-06	97.7	2.172	0.068	5.52E-03	1.35E-03
68511-50-2	y=3	8.81E-03	1.13E-03	97.7	2.172	0.068	5.52E-03	5.32E-04
68511-50-2	y=8	1.31E-11	6.96E-11	97.8	2.172	0.068	5.52E-03	3.80E-13
68515-88-8	y=1	0.03	2.47E-06	97.7	2.172	0.068	5.52E-03	1.87E-03
68515-88-8	y=4	1.88E-10	3.04E-16	97.8	2.172	0.068	5.52E-03	5.57E-12
67762-55-4	y=2.5, x=1	3.84E-06	1.10E-11	97.8	2.172	0.068	5.52E-03	1.91E-07
67762-55-4	y=2.5 x=2	3.30E-07	1.24E-12	97.8	2.172	0.068	5.52E-03	1.55E-08

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HERTG HPV Group 1 - Alkyl Sulfides Category

Table 3: Environmental Fate of Representative Structures of Alkyl Sulfides as Modeled by EQC Level II

CAS #	N	Air % degraded	Water % degraded	Soil % degraded	Sediment % degraded
67124-09-8	Monomer	91.5	nil	nil	nil
72162-15-3	Dimer, S	96.9	0.002	nil	nil
72162-15-3	Dimer, SS	99.1	nil	nil	nil
68511-50-2	Y=3	92.7	nil	nil	nil
68511-50-2	Y=8	nil	nil	nil	nil
68515-88-8	Y=1	89.7	nil	nil	nil
68515-88-8	Y=4	nil	nil	0.002	nil
67762-55-4	Y=2.5, x=1	3.47	nil	0.002	nil
67762-55-4	Y=2.5 x=2	1.04	nil	0.002	nil